

## PATENT ABSTRACTS OF JAPAN

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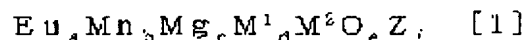
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(54) FLUORESCENT SUBSTANCE, LIGHT EMITTING SYSTEM, ILLUMINATING SYSTEM AND IMAGE-DISPLAYING SYSTEM USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fluorescent substance that gives high color rendering properties and develops deep red or white color and provide a light emitting system that is produced by using the fluorescent substance and can strongly emit visible light.

SOLUTION: The fluorescent substance includes the crystal phase having the chemical composition represented by formula [1] (wherein M1 is a monovalent element or a divalent elements except Eu, Mn and Mg wherein the divalent elements occupies >80 mol%, the total of Ba, Ca and Sr is >40 mol% and the molar ratio of Ca to the total of Ba+Ca is <0.2; M2 is a tetravalent element group including Si and Ge in an amount of >90 mol% in total; Z is a monovalent element, a divalent element, H or N; a, b, c, d, e, and f are each 0.0003<math>\leq a \leq 0.01</math>, 0<math>b < 0.075</math>, 0<math>c/(c+d) \leq 0.8</math>, 1.8<math>\leq (a+b+c+d) \leq 2.2</math>, 0<math>\leq f/(e+f) \leq 0.035</math>, 3.6<math>\leq (e+f) \leq 4.4</math>). The light emitting system is prepared by combining the fluorescent substance with a light source for radiating the light of 350 to 430 nm wavelength.



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**CLAIMS**

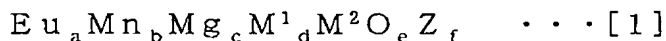

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[Claim(s)]

[Claim 1]

A fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1].

[Formula 1]



(However, the divalent element excluding [ M<sup>1</sup> ] a univalent element, Eu, Mn, and Mg, a trivalent element, and pentavalence)

The rate that expresses at least one sort of elements chosen from the group of an element, and a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the rate (mole ratio) of Ca to the sum total of Ba and Ca is less than 0.2. M<sup>2</sup> is Si and G.

e -- the sum total -- more than 90mol% -- expressing the included tetravalent element group, Z is at least one sort of elements chosen from the group which consists of the element of -1 value and -2 value, H, and N. 0 < b < 0.075, c, and d are numbers with which a is satisfied with of 0.0003 <= a <= 0.01, and 1.8 <= (a+b+c+d) <= 2.2, e, and f are [ b / 0 < c / (c+d) <= 0.8, a, b, c, and d ] satisfied of 0 <= f / (e+f) <= 0.035 and 3.6 <= (e+f) <= 4.4.

[Claim 2]

It is the feature about a rate that the sum total of Ba, Ca, and Sr occupies in M<sup>1</sup> being more than 80mol%.

The fluorescent substance according to claim 1 to carry out.

[Claim 3]

It indicates to 1, wherein a rate that Si occupies in M<sup>2</sup> is more than 80mol%, or 2.

\*\*\*\*\*.

[Claim 4]

The 1st photogen that generates light of 350 to 430 nm.

The 2nd photogen that generates visible light by the exposure of light from the 1st photogen concerned.

It is the luminescent device provided with the above, and the 2nd photogen contains a fluorescent substance of a statement in any 1 paragraph of claims 1-3.

[Claim 5]

The luminescent device according to claim 4, wherein the 1st photogen is a laser diode or a light emitting diode.

[Claim 6]

A lighting system which has the luminescent device according to claim 4 or 5.

[Claim 7]

An image display device which has the luminescent device according to claim 4 or 5.

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[Translation done.]

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### DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

In this invention, the parent compound which absorbs the light in ultraviolet radiation or a light range, and emits the visible light of long wavelength makes the 2nd photogen the fluorescent substance containing an activation element, and it, and combines the 1st photogen and 2nd photogen that emit light in the light of a light range from ultraviolet radiation by a power source.

Therefore, it is related with the luminescent device which cannot be based on an operating environment but can be made to generate luminescence of high intensity.

[Background of the Invention]

[0002]

The fluorescent substance which the fluorescent substance of a large number which emit light in red by ultraviolet radiation is known conventionally, and emits light white is also known. It mixes with the fluorescent substance of other luminescent color as an object for lighting, and a red fluorescent substance is used as white. In these, the fluorescent substance with easily stable manufacture is an oxide which S and halogen hardly contain. The oxide which S and halogen hardly contain is an oxide S under crystal and whose content of a halogen are less than 2mol% as below an impurity level, i.e., a rule of thumb. C [ say / are because an oxide which is called  $\text{La}_2\text{O}_2\text{S}:\text{Eu}$  and which contains S as crystal constituent elements is not ultraviolet radiation exposure Sadamu Tokiyasu under existence of the water in the atmosphere or the air, and /  $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}):\text{Sb}$  and Mn ]

It is because the oxide which contains halogen, such as I, as crystal constituent elements has concern of corrosion at the time of manufacture and manufacture is not easy. They are  $Y_2O_3:Eu$  and  $Y(P, V)O_4:Eu$  (Sr, M) as a fluorescent substance which emits light in red in the oxide which S and halogen hardly contain,

g)  $\text{YVO}_4:\text{Dy}$  is mentioned as a fluorescent substance in which  ${}^3(\text{PO}_4)_2:\text{Sn}$  emits light white. (For example, it is indicated in the fluorescent substance handbook (the volume for fluorescent substance said societies, Ohm-Sha, 1987)). The above-mentioned red fluorescent substance emits light by the f-f transition process of  $\text{Eu}^{3+}$ , and since a line spectrum is given, even if it combines blue and a green fluorescent substance with this, only color-rendering low white light is acquired. Color rendering properties are one of the factors made into a problem, when mixing the different luminescent color and generating white light.

Although it is a measure showing how near how where the color of the object illuminated with the light which a fluorescent substance emits to how where the color of the object illuminated by sunlight is in sight is, it is in the tendency for color rendering properties to become high, so that the half breadth of the emission spectrum of a fluorescent substance becomes large.

In the spectrum compounded when mixing red and a green and blue fluorescent substance, generating white light and red light emission peak width was small, A big valley will be able to be made to between green peaks (i.e., the field of 550 to 590 nm), and it will not be able to be made in agreement with the sunlight spectrum which does not have a valley in the field, but color rendering properties will become low. It is difficult for half breadth to acquire color-rendering high white light from this reason with a red fluorescent substance which is less than 20 nm and which is called  $Y_2O_3:Eu$  and  $Y(P, V)O_4:Eu$  which emit a line spectrum.

(Sr, Mg) With a red fluorescent substance called  $_2(\text{PO}_4)_2\text{Sn}$ , it is 254-nm mercury of a conventional type.

Although light is emitted by luminescent line excitation, depending on the powerful source of long wavelength light of the GaN system semiconductor developed in recent years, light is hardly emitted, but an excitation source is limited extremely, and it is not satisfactory. About the above-mentioned white fluorescent substance, color rendering properties are low. This carries out white light with the blue near 480 nm and the yellow near 570 nm in complementary color relation.

Since a red component and the green component are insufficient, color rendering properties are low.

Thus, the conventional red which S and halogen hardly contain and a white fluorescent substance, Since a red light ingredient, with the light source the problem that good color rendering properties or vividness cannot be given, or near 400 nm.

[0003]

The red or the white fluorescent substance which S and halogen hardly contain in recent years, . Combined with the GaN system semiconductor which emits a near-ultraviolet light with powerful intensity by the low voltage. It is  $Y_2$  although  $Y_2O_3:Eu$  is mentioned as an example in case the fluorescent substance which power consumption is proposed as a light source of a small long lasting image display device or a lighting system, and the luminescent device of white light combines is a red fluorescent substance.

O<sub>2</sub>: White obtained when Eu, blue and a green phosphor, and a near-ultraviolet light light source are combined

Since the emission spectrum of  $Y_2O_3:Eu$  is a line spectrum, the color rendering properties of light are the same reasons

as point \*\*.

\*\* et al. -- it is low and luminescence intensity is also low. As an example in case the fluorescent substance to combine is a white fluorescent substance, the method of using an phosphate and/or a borate salt fluorescent substance for JP,2002-359404,A is shown. However, in this method, the emission spectrum wide enough which came to the red field is not obtained from blue, color rendering properties are low and the vivid luminescent color is not obtained. As other red fluorescent substances, they are  $\text{CaSiO}_3$ -b, Mn, S:Cu (Zn, Cd), and aluminum (Zn, Cd).

Although there were S:Ag etc., since poisonous Cd, Pb, etc. were used, it becomes a factor which worsens a living environment and development of the fluorescent substance which does not use such an element was desired.

[0004]

It is required that the luminosity in a temperature higher than a room temperature of the fluorescent substance combined with a GaN system semiconductor should also be high enough since the temperature near a fluorescent substance becomes higher than a room temperature by generation of heat of a semiconductor at the time of use. Since red that the conventional manufacture is easy and stable type, and the lighting system and image display device incorporating a white fluorescent substance have the insufficient peak of a deep red ingredient like \*\*\*, a skillful light of high color rendering properties is not obtained, and cannot be satisfied.

[Patent documents 1] JP,2002-359404,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0005]

this invention gives high color rendering properties and vividness in view of the above-mentioned conventional technology -- in other words. It is a fluorescent substance which gives the red which gives a wide light emission peak including the red ingredient which is bright and is deep or the white fluorescent substance of a 615-645nm field, and red or white luminescence in which both color rendering properties and intensity are high combining the source of a near-ultraviolet light especially. the purpose -- and temperature characteristics are good, manufacture is easy, and it is providing a stable fluorescent substance.

[Means for Solving the Problem]

[0006]

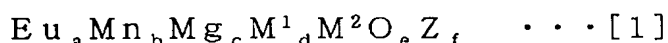
As a result of inquiring wholeheartedly that said technical problem should be solved, this invention person has large half breadth, and gives a red light peak which has a peak top between 615-645nm, Or the red peak is a fluorescent substance which gives an emission spectrum over a blue field which has big width very much from the first, And in response to an exposure of light of 350 to 430 nm, it is activated from low-concentration Eu and Mn, and there is specifically no Ca about red or a fluorescent substance which emits light strongly white, or  $\text{M}_2\text{SiO}_4$  type silicate which is below a small quantity and contains Ba and Mg was found out, and this invention was reached. Especially a fluorescent substance of this invention emits light strongly with every light source which is in a huge wavelength area over 400-nm \*\*\*\*\* from near 250 nm, and is sensed bright, is based on deep red, emits skillful visible light, and has the feature that temperature characteristics are good.

[0007]

Namely, the 1st photogen that this invention makes a fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1] the first gist, and generates light of 350 to 430 nm, Let a luminescent device with which said 2nd photogen is characterized by being a fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1] be the second gist in a luminescent device which has the 2nd photogen that generates visible light by the exposure of light from the 1st photogen concerned.

[0008]

[Formula 1]



[0009]

(However, the divalent element excluding [  $\text{M}^1$  ] a univalent element, Eu, Mn, and Mg, a trivalent element, and pentavalence)

The rate that expresses at least one sort of elements chosen from the group of an element, and a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the rate (mole ratio) of Ca to the sum total of Ba and Ca is less than 0.2.  $\text{M}^2$  is Si and G.

e -- the sum total -- more than 90mol% -- expressing the included tetravalent element group, Z is at least one sort of elements chosen from the group which consists of the element of -1 value and -2 value, H, and N.  $0 < b < 0.075$ , c, and d are numbers with which a is satisfied with of  $0.0003 \leq a \leq 0.01$ , and  $1.8 \leq (a+b+c+d) \leq 2.2$ , e, and f are  $[b / 0 < c / (c+d) \leq 0.8]$ , a, b, c, and d ] satisfied of  $0 \leq f / (e+f) \leq 0.035$  and  $3.6 \leq (e+f) \leq 4.4$ .

[Effect of the Invention]

[0010]

According to this invention, high color rendering properties are given, deep red or color rendering properties are high, and even if it exceeds a room temperature with skillful white fluorescent substances and those features, the luminescent device which emits strong visible light can be provided.

[Best Mode of Carrying Out the Invention]

[0011]

Hereafter, although an embodiment of the invention is described in detail, this invention is not limited to following embodiments, within the limits of the gist, can change variously and can be carried out.

A luminescent device this invention is characterized by that comprises the following.

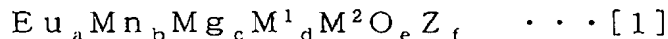
The fluorescent substance which is a fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1], and has a crystal phase which has the chemical composition of a

following general formula [1].

The light source for making it irradiate with the light of 350 to 430 nm.

[0012]

[Formula 2]



[0013]

The divalent element excluding [ M<sup>1</sup> in a formula [1] ] a univalent element, Eu, Mn, and Mg, a trivalent element, At least one sort of elements chosen from the group of a pentavalent element are expressed, the rate that a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the conditions comparatively (mole ratio) of less than 0.2 of Ca to the sum total of Ba and Ca are fulfilled. When elements other than Ba, Ca, and Sr are described concretely, as a univalent element, They are mentioned by Li, Na, K, Rb, Cs, etc. and as a divalent element, V, Cr, Fe, Co, nickel, Cu, Zn, Mo, Ru, Pd, Ag, Cd, Sn, Sm, Tm, Yb, W, Re, Os, Ir, Pt, Hg, Pb, etc. are mentioned, Although rare earth elements, such as B, aluminum, Ga, In, etc. Y, Sc, are mentioned and P, Sb, Bi, etc. are mentioned as a pentavalent element as a trivalent element, it is not limited to these. In a divalent element, V, Zn, Mo, Sn, Sm, Tm, Yb, W, and Pb are mentioned especially.

[0014]

A join of silicate by diffusion in a solid at the time of calcination of an element divalent [ in M<sup>1</sup> ] and activation element Eu<sup>2+</sup>, and Mn<sup>2+</sup>

In a meaning which helps crystallization, univalent and a trivalent and pentavalent element may be introduced less than [ sum total 20mol% ]. Less than 0.1 have a preferred rate (mole ratio) of Ca to the sum total of Ba and Ca, and 0 is more preferred in fields, such as a deep red ingredient. A thing of Ca to the sum total of Ba and Ca for which 0 is exceeded comparatively (mole ratio) is preferred, and 0.1 or more are more preferred in a field which had complete set of blue peak, green peak, and red peaks of both at a sufficient rate of obtaining a color-rendering, very high visual spectral line.

[0015]

It is preferred that a rate that the sum total of Ba, Ca, and Sr occupies from fields, such as red or white luminescence intensity, is more than 80mol%, It is more preferred that a rate that the sum total of Ba and Ca occupies is more than 80mol%, and it is still more preferred that Ba, Ca, and the percentage that the sum total of Sr occupies are 100-mol%. M<sup>2</sup> in a formula [1] -- Si and germanium -- the sum total -- more than 90mol% -- an included tetravalent element group -- a table

fields, such as luminescence intensity in which \*\* is red or white, to M<sup>2</sup> -- Si -- more than 80mol% -- containing \*\*\*\* better -- it is more preferred that \*\* and M<sup>2</sup> consist of Si. As tetravalent elements other than Si and germanium Zn, Ti, Hf, etc. are mentioned and these may be included from points, such as red or white luminescence intensity, in the range which does not spoil performance.

[0016]

Z in a formula [1] is at least one sort of elements chosen from a group which consists of an element of -1 value and -2 value, H, and N, For example, in addition to S, Se, and Te which are the elements of the same -2 value as oxygen, it may be F, Cl, Br, I, etc. which are -1 value, an OH radical may contain, and some oxygen groups may change to ON group or N basis. Z -- the grade 2 [ about ] with little influence for fluorescence performance, i.e., an elemental ratio for all of an impurity level, -- it may be contained at less than mol%. This is equivalent to 0.035 or less as a mole ratio of Z to (Z+ oxygen atom). Therefore, it is  $0 < f/(e+f) \leq 0.035$ , from a point of performance of a fluorescent substance, as for the range of  $f/(e+f)$  which is a mole ratio of Z to (Z+ oxygen atom),  $f/(e+f) < 0.01$  is preferred, and  $f/(e+f) = 0$  is preferred [ the range ] in normal use.

[0017]

It is a number with which a is satisfied of  $0.0003 \leq a \leq 0.01$  about Eu mole-ratio [ in a formula [1] ] a. If a fluorescent substance is installed near [ this ] the chip surface in order to make a fluorescent substance emit light efficiently although skin temperature of this semiconductor chip exceeds 100 \*\* at the time of an operation when using a GaN system semiconductor as the 1st light source, temperature at the time of an operation of a fluorescent substance will be about 100 \*\*. Therefore, if service temperature of a actual fluorescent substance has a desirable fluorescent substance in which luminosity seldom falls even if it carries out a rise in heat to 100 \*\* since it is about 100 \*\* and mole-ratio a of luminescent-center-ions Eu<sup>2+</sup> is large, Since luminosity falls at temperature beyond a room temperature, by making mole-ratio a or less into 0.01, even if it carries out temperature up near 100 \*\*, luminosity does not fall, but it becomes possible to prevent a fall of temperature characteristics. When mole-ratio a of luminescent-center-ions Eu<sup>2+</sup> is too small, there is a tendency for luminescence intensity to become small, as a minimum,  $a \geq 0.001$  is more preferred and  $a \geq 0.002$  is still more preferred.

[0018]

Are a factor which influences whether Mn mole-ratio b in a formula [1] considers it as red light, or it is considered as white light, when b is 0, a red peak is not acquired but are only blue or a bluish green peak, but. If a red peak will appear in blue and a green peak, and it will become white light as a whole, if b takes a positive small value, and b takes a positive bigger value, blue and a green peak will become very small and will become main [ a red peak ]. The range of b is  $0 < b < 0.075$  as a red fluorescent substance or a white fluorescent substance. Energy of Eu<sup>2+</sup> which a fluorescent substance excited in response to an exposure of the excitation light source moves to Mn<sup>2+</sup>, Since it is thought that Mn<sup>2+</sup> is carrying out red light and a grade of energy transfer mainly changes somewhat with presentations of M<sup>1</sup> and M<sup>2</sup>, boundary values of b which changes from a red fluorescent substance to a white light fluorescent substance with the presentation of M<sup>1</sup> and M<sup>2</sup> differ somewhat. So, although the good range of b of red light and white light is strictly

undistinguishable, from fields, such as intensity of the luminescent color including red and white,  $0.002 \leq b < 0.075$  is more preferred, and  $0.005 \leq b < 0.075$  is still more preferred. It shall be interpreted by broad sense, the two or more maximal value exists in an emission spectrum, and "white" as used in this invention means that each is a broadband light emission peak.

[0019]

Although dyad is replaced by the main  $M^1$  and  $c/(c+d)$  which is a rate of the number of mols of Mg and Mg to the number of sum total mols of  $M^1$  is  $0 < c/(c+d) \leq 0.8$ , Mg in a formula [1], from fields, such as red or white luminescence intensity,  $c/(c+d) \leq 0.7$  is preferred.

In crystal phase  $Eu_a Mn_b Mg_c M^1_d M^2_e O_f Z_f$  of said general formula [1],  $Eu^{2+}$ ,  $Mn^{2+}$ , and  $Mg^{2+}$  are replaced by  $M^1$  which mainly consists of dyads, Although  $M^2$  is mainly occupied in Si and germanium, an anion is mainly oxygen and  $M^1$ ,  $M^2$ , and the total mole ratio of an oxygen atom of the basic composition are the things of 2, 1, and 4, respectively, It is 1 \*\*\*\* on a chemical formula about all the mole ratios of  $M^2$  which Si and germanium mainly occupy since there is no big influence in fluorescence performance of this purpose even if a cation deficit and an anion deficit have arisen somewhat.

When [ constant ] it carries out, a mole ratio  $(a+b+c+d)$  of  $(M^1+Eu+Mn+Mg)$  is  $1.8 \leq$ .

It is the range of  $a+b+c+d \leq 2.2$  and it is preferred that it is  $\approx 2$  especially  $(a+b+c+d)$ . all the mole ratios of a site by the side of an anion — it is  $(e+f)$  — it is the range of  $3.6 \leq (e+f) \leq 4.4$ , and it is usually preferred that it is  $e = 4$  and  $f = 0$  especially.

[0020]

A fluorescent substance used by this invention can be manufactured by heat-treating and calcinating a mixture which prepared a source of  $M^1$  as shown in said general formula [1], a source of  $M^2$ , a source of Mg, and a source compound of an element of Eu and Mn that is activation elements with a mixed method of the following (A) or (B).

(A) A dry-blending method with which dry mills, such as a hammermill, a roll mill, a ball mill, and a jet mill, or a mortar, grinding using a pestle etc., and mixers, such as a ribbon blender, a V type blender, and a Henschel mixer, or a mortar and mixing using a pestle were doubled.

(B) A wet-blending method which adds water etc., is mixed with a grinder, a mortar and a pestle, an evaporating dish, a rabble, etc. by a slurry regime or solution states using a grinder, a mortar, a pestle, etc., and is dried by spray drying, stoving, or natural seasoning.

[0021]

Especially in a source compound of an element of an activation element in these mixed methods, It is preferred to use a liquid medium, since it is necessary to make the whole mix and distribute a little compounds uniformly, Also from a field where uniform mixing is obtained by the whole in other source compounds of an element, latter wet process is preferred and as a heat-treating method, In heat-resistant containers, such as alumina, crucible made from quartz, and a tray, it is  $900-1400$  \*\* in temperature preferably, and  $750-1500$  \*\* is usually made by gases, such as the atmosphere, oxygen, carbon monoxide, carbon dioxide, nitrogen, hydrogen, and argon, being independent, or heating under a mixed atmosphere for 10 minutes – 24 hours. Washing, desiccation, classifying processing, etc. are made after heat-treatment if needed.

[0022]

An atmosphere required in order to acquire an ionic state (valence) which an activation element contributes to luminescence as said heated atmosphere is chosen. In the case of divalent Eu, Mn, etc. in this invention, the bottom of the neutrality of carbon monoxide, nitrogen, hydrogen, argon, etc. or reducing atmosphere is preferred, but it is possible if the bottom of oxidizing atmospheres, such as the atmosphere and oxygen, also chooses even conditions.

Here, as a source of  $M^1$ , a source of  $M^2$ , a source of Mg, and a source compound of an element of an activation element, it is  $M^1$ .

Each oxide of  $M^2$ , Mg, and an activation element, hydroxide, carbonate, a nitrate, sulfate, an oxalate, Carboxylate, a halogenide, etc. are mentioned and it is chosen in consideration of un-generating nature, such as reactivity to a multiple oxide out of these and  $NO_x$  at the time of calcination, and  $SO_x$ , etc.

[0023]

If those source compounds of  $M^1$  are concretely illustrated about said Ba currently mentioned as  $M^1$ , Ca, and Sr, as a source compound of Ba, they will be  $BaO$ ,  $Ba(OH)_2$  and  $8H_2O$ , and  $BaCO_3$ .

$Ba(NO_3)_2$ ,  $BaSO_4$ ,  $Ba(OCO)_2$  and  $2H_2O$ ,  $Ba(OCOCH_3)_2$ , B

$aCl_2$  etc. are  $CaO$ ,  $Ca(OH)_2$ ,  $CaCO_3$ , and Ca as a source compound of Ca again.

$NO_{32}$  and  $4H_2O$ ,  $CaSO_4$  and  $2H_2O$ ,  $Ca(OCO)_2$  and  $H_2O$ ,  $Ca(OCOCH_3)_2$  and  $H_2O$ ,  $CaCl_2$ , etc. again as a source compound of Sr,  $SrO$ ,  $Sr(OH)_2$  and  $8H_2O$ ,  $SrCO_3$ ,  $Sr(NO_3)_2$ ,  $SrSO_4$ ,  $Sr(OCO)_2$  and  $H_2O$ ,  $Sr(OCO)$

$CH_{32}$  and  $0.5H_2O$ ,  $SrCl_2$ , etc. are mentioned, respectively.

[0024]

if those source compounds of  $M^2$  are concretely illustrated about said Si currently mentioned as  $M^2$ , and germanium — a Si-source compound — carrying out —  $SiO_2$ ,  $H_4SiO_4$ ,  $Si(OCOCH_3)_4$ , etc. — moreover

a source compound of germanium — carrying out —  $GeO_2$ , germanium(OH)<sub>4</sub>, germanium(OCOCH<sub>3</sub>)<sub>4</sub>,  $GeCl_4$ , etc.

\*\*\*\*\*

If a source compound of Mg is concretely illustrated about Mg, they will be  $MgO$ ,  $Mg(OH)_2$ , and  $MgC$ .

$O_3$ ,  $Mg(OH)_2$  and  $3MgCO_3$ , and  $3H_2O$ ,  $Mg(NO_3)_2$  and  $6H_2O$ ,  $MgSO_4$ ,  $Mg(OCO)_2$  and  $2H_2O$ ,  $Mg(OCOCH_3)_2$  and  $4H_2O$ ,  $MgCl_2$ , etc. are mentioned, respectively.

[0025]

If the source compound of an element is concretely illustrated about said Eu and Mn which are mentioned as an activation element, they will be  $Eu_2O_3$ ,  $Eu_2(SO_4)_3$ ,  $Eu_2(OCO)_6$ ,  $EuCl_2$ , and  $EuCl_3$ .

$Eu(NO_3)_3$  and  $6H_2O$ ,  $Mn(NO_3)_2$  and  $6H_2O$ ,  $MnO_2$ , and  $Mn_2O_3$  and  $Mn_3O_4$

MnO, Mn(OH)<sub>2</sub>, MnCO<sub>3</sub>, Mn(OCOCH<sub>3</sub>)<sub>2</sub> and 2H<sub>2</sub>O, Mn(OCO)  
CH<sub>33</sub> and nH<sub>2</sub>O, MnCl<sub>2</sub>, 4H<sub>2</sub>O, etc. are mentioned.

[0026]

In this invention, the 1st photogen that irradiates said fluorescent substance generates light of 350 to 430 nm wavelength. A photogen which generates light which has peak wavelength is preferably used for the range of 350 to 430 nm wavelength. As an example of the 1st photogen, a light emitting diode (LED) or a laser diode (LD) can be mentioned. It is a laser diode more preferably at a point which has them. [ little power consumption ] [ good power consumption, and ] In it, the GaN systems LED and LD which use a GaN system compound semiconductor are preferred. It is because it compares with SiC system LED etc. which emit light of this field, and a radiant power output and external quantum efficiency boil the GaN systems LED and LD markedly, and are large and very bright luminescence is dramatically obtained with low electric power by combining with said fluorescent substance. For example, a GaN system usually has luminescence intensity of 100 times or more of a SiC system to 20-mA current load. In the GaN systems LED and LD, what has an aluminum<sub>x</sub>Ga<sub>y</sub>N luminous layer, a GaN luminous layer, or an In<sub>x</sub>Ga<sub>y</sub>N luminous layer is preferred. In GaN system LED, since what has an In<sub>x</sub>Ga<sub>y</sub>N luminous layer in them is dramatically strong as for luminescence intensity, it is especially desirable, and in GaN system LD, since the thing of luminescence intensity of multiple quantum well structure of an In<sub>x</sub>Ga<sub>y</sub>N layer and a GaN layer is dramatically strong, it is especially desirable. In the above, a value of X+Y is usually a value of the range of 0.8-1.2. In GaN system LED, when what doped Zn and Si to these luminous layers, and what has a nothing dopant adjust a luminescent characteristic, it is desirable. GaN system LED uses these luminous layers, p layer, a n layer, an electrode, and a substrate as a basic building block. A luminous layer An aluminum<sub>x</sub>Ga<sub>y</sub>N layer of a n type and a p type, a GaN layer, Or what has the hetero structure made sandwiches in an In<sub>x</sub>Ga<sub>y</sub>N layer etc. is high, its luminous efficiency is preferred, and what made hetero structure quantum well structure further has still higher luminous efficiency, and is more preferred.

[0027]

In this invention, since luminous efficiency of the whole luminescent device will be raised, it is especially preferred to use a photogen of a surface-emitting type, especially a surface-emitting type GaN system laser diode as the 1st photogen. A photogen of a surface-emitting type is a photogen which has luminescence strong against a membranous plane direction, and luminescence of a plane direction can be made stronger than the direction of an edge of a luminous layer in a surface-emitting type GaN system laser diode by controlling crystal growth, such as a luminous layer, and devising a reflecting layer etc. well. It compares with a type which emits light from an edge of a luminous layer by using a thing of a surface-emitting type. Since an irradiation surface product can be dramatically enlarged with the same light volume and irradiation efficiency can be improved when irradiating a fluorescent substance of the 2nd photogen with the light, as a result of a luminescence cross-section area per unit light quantity being able to take greatly, stronger luminescence can be obtained from a fluorescent substance which is the 2nd photogen.

[0028]

When using a thing of a surface-emitting type as the 1st photogen, it is preferred to make the 2nd photogen into the shape of a film. As a result, since an irradiation cross section product to a fluorescent substance from the 1st photogen will become large per fluorescent substance unit quantity if the 2nd photogen is carried out in the direction of the section with the shape of a film, since the cross-section area is large enough, the light from a photogen of a surface-emitting type can enlarge intensity of luminescence from a fluorescent substance more.

When using a thing of a surface-emitting type as the 1st photogen and using a film-like thing as the 2nd photogen, it is preferred to consider it as shape which contacted the direct film-like 2nd photogen to a light-emitting surface of the 1st photogen. Contact here means building the state where it has touched exactly without the 1st photogen's and 2nd photogen's passing air and a gas. As a result, since light volume loss that it is reflected by a film surface of the 2nd photogen, and light from the 1st photogen oozes outside is avoidable, luminous efficiency of the whole device can be improved.

[0029]

A typical perspective view showing physical relationship of the 1st photogen and the 2nd photogen in an example of a luminescent device of this invention is shown in drawing 1. The film-like 2nd photogen in which one in drawing 1 has said fluorescent substance, and 2 express surface-emitting type GaN system LD as the 1st photogen, and three express a substrate. In order to build the state where it contacted mutually, separate \*\* is built with LD2 and the 2nd photogen 1, respectively, and those fields may be contacted by adhesives or other means, and it is the 2nd photogen on a light-emitting surface of LD2.

A film may be made to produce (molding). These results can change LD2 and the 2nd photogen 1 into the state where it contacted.

[0030]

Although light from the 1st light and 2nd photogen from a photogen is usually suitable in all directions, since the part will be reflected when light comes out of resin if powder of a fluorescent substance of the 2nd photogen is distributed in resin, direction of light can be arranged to some extent. Therefore, since light can be derived to some extent in the efficient direction, it is preferred to use what distributed powder of said fluorescent substance into resin as the 2nd photogen. Since all the irradiation surface products to the 2nd photogen of light from the 1st photogen will become large if a fluorescent substance is distributed in resin, it also has an advantage that luminescence intensity from the 2nd photogen can be enlarged. In this case, as resin which can be used, although various kinds of things, such as silicon resin, an epoxy resin, polyvinyl system resin, polyethylene system resin, a polypropylene resin, and polyester system resin, are mentioned, the dispersibility of phosphor powder is silicon resin or an epoxy resin preferably at a good point. When distributing powder of the 2nd photogen in resin, a weight ratio of powder of the 2nd photogen concerned and its the whole resin powder is 10 to 95% of usually 30 to 80% still more preferably 20 to 90% preferably. When there are too many fluorescent substances, luminous efficiency may fall by condensation of powder, and when too small, luminous efficiency may fall shortly for the absorption of light by resin, or dispersion.

[0031]

Come to comprise a luminescent device of this invention said fluorescent substance as a wavelength conversion material, and a light emitting device which generates light of 350 to 430 nm, and said fluorescent substance absorbs light of 350 to 430 nm which a light emitting device emits. A fluorescent substance which has a crystal phase of this

invention which is not based on an operating environment, but color rendering properties are good, and are the luminescent devices which can be made to generate visible light of high intensity, and constitutes a luminescent device. By the exposure of light from the 1st photogen that generates light of 350 to 430 nm, light is emitted to a wavelength area showing red or white. And a luminescent device of this invention fits light sources, such as lighting systems, such as image display devices, such as a light source of a back light source, a signal, etc., and a color liquid crystal display, and surface light.

[0032]

When a luminescent device of this invention is explained based on a drawing, drawing 2. It is a typical sectional view showing one example of a luminescent device which has the 1st photogen (350–430nm photogen) and 2nd photogen, 4 — as for the 1st photogen (photogen of 350 to 430 nm), and 8, a mount lead and 6 are [ a conductive wire and 10 ] molding members a fluorescent substance content resin part as the 2nd photogen, and 9 an inner lead and 7 a luminescent device and 5.

[0033]

As shown in drawing 2, make a luminescent device which is an example of this invention, and a general artillery shell type gestalt in a top cup of the mount lead 5, The 1st photogen (350–430nm photogen) 7 that consists of a GaN system light emitting diode etc., Moreover mixes and distributes a fluorescent substance to binders, such as silicon resin, an epoxy resin, and an acrylic resin, and it is being fixed by slushing in a cup by being covered with the fluorescent substance content resin part 8 formed as the 2nd photogen. On the other hand, it has flowed through the photogen 7, the mount lead 5, and the 1st photogen 7 and inner lead 6 in the conductive wire 9, respectively, and these whole is covered with the molding member 10 by an epoxy resin etc., and it comes to protect them. [ 1st ]

[0034]

The surface light lighting system 11 incorporating this light emitting device 1, As shown in drawing 3, an inner surface on the bottom of the holding case 12 of a rectangle made into light impermeability nature, such as a white smooth side. A power supply, a circuit (not shown), etc. for a drive of many luminescent devices 13 of the luminescent device 13 on the outside are provided and arranged, and the diffusion boards 14, such as an acrylic board made into opalescence, are fixed to a part equivalent to a covering device of the holding case 12 for equalization of luminescence.

[0035]

And drive the surface light lighting system 11, and light of 350 to 430 nm is made to emit light by impressing voltage to the 1st photogen of the light emitting device 13, and let a part of the luminescence be the 2nd photogen.

Said fluorescent substance in a fluorescent substance content resin part of \*\* absorbs, emit light in visible light, on the other hand, color-rendering high luminescence is obtained with mixed colors with blue glow etc. which were not absorbed by fluorescent substance, and this light penetrates the diffusion board 14, It will be emitted to the drawing upper part and illumination light of a uniform luminosity will be obtained in the 14th page of a diffusion board of the holding case 12.

[0036]

Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples, unless the gist is exceeded.

[Work example 1]

[0037]

Solution of  $\text{Ba}(\text{NO}_3)_2$ , solution of  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ , Solution of  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , solution of  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , Solution of  $\text{Mn}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , and suspension of colloidal silica ( $\text{SiO}_2$ ) (it  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , S

The mole ratio of  $\text{SiO}_2$  is platinum about 1.218:0.23:0.512:0.01:0.03:1.

It mixes in a container, calcinates after desiccation by heating for 2 hours by 1050 \*\* of nitrogen gas flowing down containing 4% of hydrogen, and is fluorescent substance  $\text{Ba}_{1.218}\text{Ca}_{0.23}\text{Mg}_{0.512}\text{Eu}_{0.01}\text{Mn}_{0.03}\text{SiO}_4$  (the 2nd).

The fluorescent substance used for a photogen was manufactured. The emission spectrum when this fluorescent substance was excited at 400 nm which is the dominant wavelength of the ultraviolet radiation field of a GaN system light emitting diode was measured. Intensity when wavelength of the peak of the red component and intensity of the peak of the red component of the below-mentioned comparative example 2 are set to 100 table-1. . Receive, when luminosity under (it being hereafter called relative intensity), half breadth, and a room temperature (23 \*\*) is set to 1. The rate of the luminosity under 80 \*\* supposing the operating state at the time of making light emit combining this fluorescent substance and a GaN system light emitting diode and 100 \*\*, x value of a chromaticity coordinate, y value, and the half breadth of a peak group are shown. Since this fluorescent substance has intensity and large half breadth enough, it turns out that it is the skillful white light which gives high color rendering properties, and contains a skillful deep red ingredient since it is in the field whose peak wavelength is 615 to 645 nm. When it combines with a GaN system semiconductor, it turns out that luminosity even with a temperature of nearly 100 \*\* unchanging with a room temperature to produce is given.

[0038]

The peak of a red component refers to the peak in the not less than 590-nm field in an emission spectrum. Which serves as a rule of thumb to which it is broadly distributed over and which gets to know whether color rendering properties are high, and an emission spectrum defines the half breadth of a peak group as the total of the width of a wavelength area which has the intensity more than half of the intensity of the maximum peak in an emission spectrum like drawing 4.

(Comparative example 1)

The solution of  $\text{Ba}(\text{NO}_3)_2$ , the solution of  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ , The solution of  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , the solution of  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , And suspension of colloidal silica ( $\text{SiO}_2$ ) (it  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , Except the mole ratio of  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , and  $\text{SiO}_2$  teaching 1.187:0.396:0.198:0.2:0.02:1, and using it as an undiluted solution, Fluorescent substance  $\text{Ba}_{1.187}\text{Ca}_{0.396}\text{Mg}_{0.198}\text{Eu}_{0.2}\text{Mn}_{0.02}\text{SiO}_4$  was manufactured like Example 1.

GaN system luminescence rhei rhizoma

The emission spectrum when this fluorescent substance was excited at 400 nm which is the dominant wavelength of the ultraviolet radiation field of DO was measured. . Receive table-1, when wavelength of the peak of the red



component, relative intensity, half breadth, and luminosity under a room temperature (23 \*\*) are set to 1. The rate of the luminosity under 80 \*\* supposing the operating state at the time of making light emit combining this fluorescent substance and a GaN system light emitting diode and 100 \*\*, x value of a chromaticity coordinate, y value, and the half breadth of a peak group are shown. When Eu mole ratio is enlarged with 0.01 to 0.2, it turns out that the luminosity under 80 \*\* or 100 \*\* falls compared with the bottom of a room temperature.

(Comparative example 2)

The solution of  $\text{Ba}(\text{NO}_3)_2$ , the solution of  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ , The solution of  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , the solution of  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , Solution of  $\text{Mn}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , and suspension of colloidal silica ( $\text{SiO}_2$ ) (it  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , S

The mole ratio of  $\text{SiO}_2$  is \*\*\*\* about 1.144:0.216:0.48:0.01:0.15:1.

Fluorescent substance  $\text{Ba}_{1.144}\text{Ca}_{0.216}\text{Mg}_{0.48}\text{Eu}_{0.01}\text{Mn}_{0.15}\text{SiO}_4$  was manufactured like Example 1 except seeing and using it as an undiluted solution. The principal wave of the ultraviolet radiation field of a GaN system light emitting diode The emission spectrum when this fluorescent substance was excited at 400 nm which is merit was measured. . Receive table-1, when wavelength of the peak of the red component, relative intensity, half breadth, and luminosity under a room temperature (23 \*\*) are set to 1. The rate of the luminosity under 80 \*\* supposing the operating state at the time of making light emit combining this fluorescent substance and a GaN system light emitting diode and 100 \*\*, x value of a chromaticity coordinate, y value, and the half breadth of a peak group are shown. In Example 1, when Mn mole ratio is enlarged with 0.03 to 0.15, it turns out that red luminescence intensity falls greatly.

(Comparative example 3)

The solution of  $\text{Ba}(\text{NO}_3)_2$ , the solution of  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ , The solution of  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , the solution of  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , And suspension of colloidal silica ( $\text{SiO}_2$ ) (it  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$  and  $4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $6\text{H}_2\text{O}$ , It is fluorescent substance  $\text{Ba}_{1.2}\text{Ca}_{0.2}\text{Mg}_{0.4}\text{Eu}$  like Example 1 except the mole ratio of  $\text{Eu}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , and  $\text{SiO}_2$  teaching 1.2:0.2:0.4:0.2:1, and using it as an undiluted solution.

$\text{Eu}_{0.2}\text{SiO}_4$  was manufactured. The emission spectrum when this fluorescent substance was excited at 400 nm which is the dominant wavelength of the ultraviolet radiation field of a GaN system light emitting diode was measured. x value of a chromaticity coordinate, y value, and the half breadth of a peak group are shown in table-1. It turns out that a not less than 590-nm peak is not seen, and a red peak does not appear unless Mn is added.

[0039]

[Table 1]

表-1

590nm以上のピーク (赤成分のピーク)	波長 (nm)	半値幅 (nm)	相対強 度	ピーク群 の半値幅 (nm)	色座標		Euの モル比	Mnの モル比	Eu,Mnを除く 2価1価3価 5価元素の 合計に対する Mgの割合 (モル比)	BaとCaの 合計に対する Caの割合 (モル比)
					x	y				
室温での輝度 に対する 100℃での 輝度の割合	623	84	256	120	0.28	0.217	0.01	0.03	0.26	0.16
0.826	595	68	642	150	0.355	0.31	0.2	0.02	0.13	0.25
0.947	632	95	100	101	0.316	0.177	0.01	0.15	0.26	0.16
-	-	-	-	73	0.199	0.476	0.2	0	0.22	0.14

実施例又は比較例	蛍光体の化学組成	室温での輝度に対する80℃での輝度の割合
実施例1	$\text{Ba}_{1.118}\text{Ca}_{0.233}\text{Mg}_{0.312}\text{Eu}_{0.01}\text{Mn}_{0.008}\text{SiO}_4$	1
比較例1	$\text{Ba}_{1.117}\text{Ca}_{0.234}\text{Mg}_{0.311}\text{Eu}_{0.01}\text{Mn}_{0.002}\text{SiO}_4$	0.947
比較例2	$\text{Ba}_{1.144}\text{Ca}_{0.219}\text{Mg}_{0.48}\text{Eu}_{0.01}\text{Mn}_{0.15}\text{SiO}_4$	0.968
比較例3	$\text{Ba}_{1.2}\text{Ca}_{0.3}\text{Mg}_{0.4}\text{Eu}_{0.5}\text{SiO}_4$	-

[Brief Description of the Drawings]

[0040]

[Drawing 1]The figure showing an example of a luminescent device which made the film-like fluorescent substance contact or mold into a surface-emitting type GaN system diode.

[Drawing 2]It is a typical sectional view showing one example of the luminescent device which comprises a fluorescent substance in this invention, and the 1st photogen (350-430nm photogen).

[Drawing 3]The typical sectional view showing an example of the surface light lighting system of this invention.

[Drawing 4]The figure showing how to measure the half breadth of a peak group.

[Description of Notations]

[0041]

- 1; the 2nd photogen
- 2; surface-emitting type GaN system LD
- 3; substrate
- 4; luminescent device
- 5; mount lead
- 6; inner lead
- 7; the 1st photogen (350-430-nm photogen)
- 8; the resin part which made the fluorescent substance in this invention contain
- 9; conductive wire
- 10; molding member
- 11; a surface light lighting system incorporating a light emitting device
- 12; holding case
- 13; luminescent device
- 14; diffusion board

[Translation done.]

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## TECHNICAL FIELD

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[Field of the Invention]

[0001]

In this invention, the parent compound which absorbs the light in ultraviolet radiation or a light range, and emits the visible light of long wavelength makes the 2nd photogen the fluorescent substance containing an activation element, and it, and combines the 1st photogen and 2nd photogen that emit light in the light of a light range from ultraviolet radiation by a power source.

Therefore, it is related with the luminescent device which cannot be based on an operating environment but can be made to generate luminescence of high intensity.

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**PRIOR ART****[Background of the Invention]****[0002]**

The fluorescent substance which the fluorescent substance of a large number which emit light in red by ultraviolet radiation is known conventionally, and emits light white is also known. It mixes with the fluorescent substance of other luminescent color as an object for lighting, and a red fluorescent substance is used as white. In these, the fluorescent substance with easily stable manufacture is an oxide which S and halogen hardly contain. The oxide which S and halogen hardly contain is an oxide S under crystal and whose content of a halogen are less than 2mol% as below an impurity level, i.e., a rule of thumb. C [ say / are because an oxide which is called  $\text{La}_2\text{O}_3\text{:Eu}$  and which contains S as crystal constituent elements is not ultraviolet radiation exposure Sadamu Tokiyasu under existence of the water in the atmosphere or the air, and /  $\text{Ca}_5(\text{PO}_4)_3(\text{F, Cl})\text{:Sb and Mn}$  ]

It is because the oxide which contains halogen, such as I, as crystal constituent elements has concern of corrosion at the time of manufacture and manufacture is not easy. They are  $\text{Y}_2\text{O}_3\text{:Eu}$  and  $\text{Y(P, V) O}_4\text{:Eu}$  (Sr, M) as a fluorescent substance which emits light in red in the oxide which S and halogen hardly contain,  $\text{g)YVO}_4\text{:Dy}$  is mentioned as a fluorescent substance in which  $\text{g(PO}_4)_2\text{:Sn}$  emits light white. (For example, it is indicated in the fluorescent substance handbook (the volume for fluorescent substance said societies, Ohm-Sha, 1987).) The above-mentioned red fluorescent substance emits light by the f-f transition process of  $\text{Eu}^{3+}$ , and since a line spectrum is given, even if it combines blue and a green fluorescent substance with this, only color-rendering low white light is acquired. Color rendering properties are one of the factors made into a problem, when mixing the different luminescent color and generating white light.

Although it is a measure showing how near how where the color of the object illuminated with the light which a fluorescent substance emits to how where the color of the object illuminated by sunlight is in sight is in sight is, it is in the tendency for color rendering properties to become high, so that the half breadth of the emission spectrum of a fluorescent substance becomes large.

In the spectrum compounded when mixing red and a green and blue fluorescent substance, generating white light and red light emission peak width was small, A big valley will be able to be made to between green peaks (i.e., the field of 550 to 590 nm), and it will not be able to be made in agreement with the sunlight spectrum which does not have a valley in the field, but color rendering properties will become low. It is difficult for half breadth to acquire color-rendering high white light from this reason with a red fluorescent substance which is less than 20 nm and which is called  $\text{Y}_2\text{O}_3\text{:Eu}$  and  $\text{Y(P, V) O}_4\text{:Eu}$  which emit a line spectrum.

(Sr, Mg) With a red fluorescent substance called  $\text{g(PO}_4)_2\text{:Sn}$ , it is 254-nm mercury of a conventional type.

Although light is emitted by luminescent line excitation, depending on the powerful source of long wavelength light of the GaN system semiconductor developed in recent years, light is hardly emitted, but an excitation source is limited extremely, and it is not satisfactory. About the above-mentioned white fluorescent substance, color rendering properties are low. This carries out white light with the blue near 480 nm and the yellow near 570 nm in complementary color relation.

Since a red component and the green component are insufficient, color rendering properties are low.

Thus, the conventional red which S and halogen hardly contain and a white fluorescent substance, Since a red light peak was thin or the wavelength was too short, there was a problem that there was no luminescence of a red ingredient, with the light source the problem that good color rendering properties or vividness cannot be given, or near 400 nm.

**[0003]**

The red or the white fluorescent substance which S and halogen hardly contain in recent years, . Combined with the GaN system semiconductor which emits a near-ultraviolet light with powerful intensity by the low voltage. It is  $\text{Y}_2\text{O}_3\text{:Eu}$  although  $\text{Y}_2\text{O}_3\text{:Eu}$  is mentioned as an example in case the fluorescent substance which power consumption is proposed as a light source of a small long lasting image display device or a lighting system, and the luminescent device of white light combines is a red fluorescent substance.

$\text{O}_3$ : White obtained when Eu, blue and a green phosphor, and a near-ultraviolet light light source are combined

Since the emission spectrum of  $\text{Y}_2\text{O}_3\text{:Eu}$  is a line spectrum, the color rendering properties of light are the same reasons as point \*\*.

\*\* et al. -- it is low and luminescence intensity is also low. As an example in case the fluorescent substance to combine is a white fluorescent substance, the method of using an phosphate and/or a borate salt fluorescent substance for JP,2002-359404,A is shown. However, in this method, the emission spectrum wide enough which came to the red field is not obtained from blue, color rendering properties are low and the vivid luminescent color is not obtained. As other red fluorescent substances, they are  $\text{CaSiO}_3\text{-b, Mn, S:Cu (Zn, Cd)}$ , and aluminum (Zn, Cd).

Although there were S:Ag etc., since poisonous Cd, Pb, etc. were used, it becomes a factor which worsens a living environment and development of the fluorescent substance which does not use such an element was desired.

**[0004]**

It is required that the luminosity in a temperature higher than a room temperature of the fluorescent substance

combined with a GaN system semiconductor should also be high enough since the temperature near a fluorescent substance becomes higher than a room temperature by generation of heat of a semiconductor at the time of use. Since red that the conventional manufacture is easy and stable type, and the lighting system and image display device incorporating a white fluorescent substance have the insufficient peak of a deep red ingredient like \*\*\*\*, a skillful light of high color rendering properties is not obtained, and cannot be satisfied.  
[Patent documents 1] JP,2002-359404,A

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## EFFECT OF THE INVENTION

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[Effect of the Invention]

[0010]

According to this invention, high color rendering properties are given, deep red or color rendering properties are high, and even if it exceeds a room temperature with skillful white fluorescent substances and those features, the luminescent device which emits strong visible light can be provided.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]

[0005]

this invention gives high color rendering properties and vividness in view of the above-mentioned conventional technology -- in other words. It is a fluorescent substance which gives the red which gives a wide light emission peak including the red ingredient which is bright and is deep or the white fluorescent substance of a 615-645nm field, and red or white luminescence in which both color rendering properties and intensity are high combining the source of a near-ultraviolet light especially. the purpose -- and temperature characteristics are good, manufacture is easy, and it is providing a stable fluorescent substance.

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**MEANS**


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[Means for Solving the Problem]

[0006]

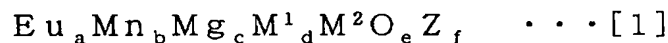
As a result of inquiring wholeheartedly that said technical problem should be solved, this invention person has large half breadth, and gives a red light peak which has a peak top between 615-645nm, Or the red peak is a fluorescent substance which gives an emission spectrum over a blue field which has big width very much from the first, And in response to an exposure of light of 350 to 430 nm, it is activated from low-concentration Eu and Mn, and there is specifically no Ca about red or a fluorescent substance which emits light strongly white, or  $M_2SiO_4$  type silicate which is below a small quantity and contains Ba and Mg was found out, and this invention was reached. Especially a fluorescent substance of this invention emits light strongly with every light source which is in a huge wavelength area over 400-nm \*\*\*\*\* from near 250 nm, and is sensed bright, is based on deep red, emits skillful visible light, and has the feature that temperature characteristics are good.

[0007]

Namely, the 1st photogen that this invention makes a fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1] the first gist, and generates light of 350 to 430 nm, Let a luminescent device with which said 2nd photogen is characterized by being a fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1] be the second gist in a luminescent device which has the 2nd photogen that generates visible light by the exposure of light from the 1st photogen concerned.

[0008]

[Formula 1]



[0009]

(However, the divalent element excluding [  $M^1$  ] a univalent element, Eu, Mn, and Mg, a trivalent element, and pentavalence)

The rate that expresses at least one sort of elements chosen from the group of an element, and a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the rate (mole ratio) of Ca to the sum total of Ba and Ca is less than 0.2.  $M^2$  is Si and G.

e — the sum total — more than 90mol% — expressing the included tetravalent element group, Z is at least one sort of elements chosen from the group which consists of the element of -1 value and -2 value, H, and N.  $0 < b < 0.075$ , c, and d are numbers with which a is satisfied with of  $0.0003 \leq a \leq 0.01$ , and  $1.8 \leq (a+b+c+d) \leq 2.2$ , e, and f are [  $b / 0 < c / (c+d) \leq 0.8$ , a, b, c, and d ] satisfied of  $0 \leq f / (e+f) \leq 0.035$  and  $3.6 \leq (e+f) \leq 4.4$ .

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[Translation done.]



\* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[0040]

[Drawing 1]The figure showing an example of a luminescent device which made the film-like fluorescent substance contact or mold into a surface-emitting type GaN system diode.

[Drawing 2]It is a typical sectional view showing one example of the luminescent device which comprises a fluorescent substance in this invention, and the 1st photogen (350-430nm photogen).

[Drawing 3]The typical sectional view showing an example of the surface light lighting system of this invention.

[Drawing 4]The figure showing how to measure the half breadth of a peak group.

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[Translation done.]

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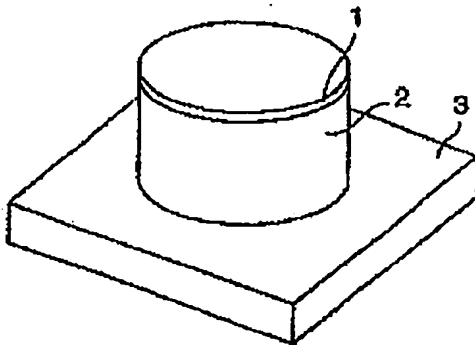
3.In the drawings, any words are not translated.

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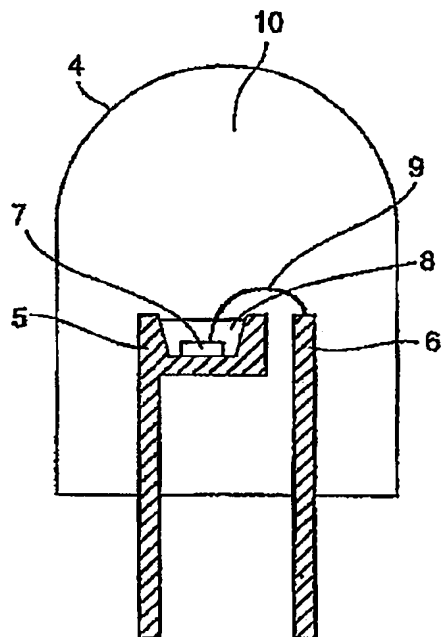
DRAWINGS

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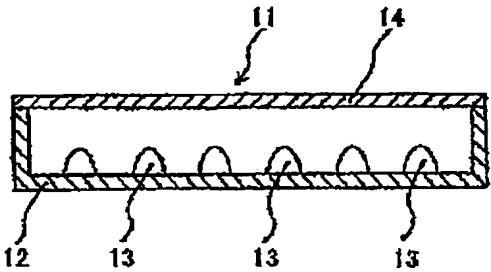
[Drawing 1]



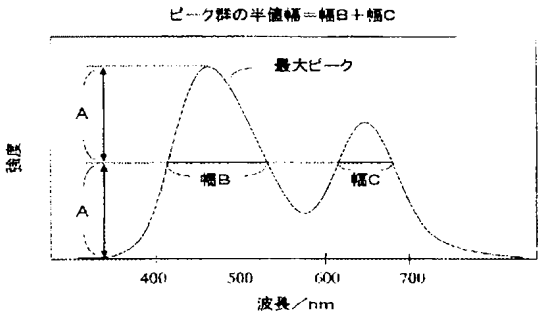
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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## CORRECTION OR AMENDMENT

[Kind of official gazette]Printing of amendment by the regulation of 2 of Article 17 of Patent Law  
 [Section classification] The 3rd classification of the part III gate  
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 [Date of Publication]July 28, Heisei 17 (2005.7.28)  
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 [Application number]Application for patent 2004-9771 (P2004-9771)  
 [International Patent Classification]

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*C09K 11/08 (2006. 01)*

*C09K 11/66 (2006. 01)*

*F21S 2/00 (2006. 01)*

*F21Y 101/02 (2006. 01)*

[FI]

C09K 11/59 CPR

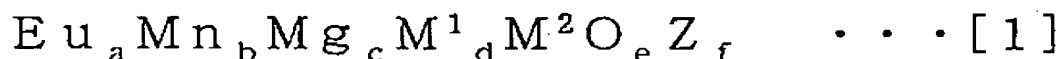
C09K 11/08 J

C09K 11/66 CPT

F21S 1/00 E

F21Y101:02

[Written amendment]  
 [Filing date]January 12, Heisei 19 (2007.1.12)  
 [Amendment 1]  
 [Document to be Amended]Claim  
 [Item(s) to be Amended]Whole sentence  
 [Method of Amendment]Change  
 [The contents of amendment]  
 [Claim(s)]  
 [Claim 1]  
 A fluorescent substance which has a crystal phase which has the chemical composition of a following general formula [1].  
 [Formula 1]



(However, the divalent element excluding [ M<sup>1</sup> ] a univalent element, Eu, Mn, and Mg, a trivalent element, the average)  
 The rate that expresses at least one sort of elements chosen as \*\* from the group of a pentavalent element, and a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the rate (mole ratio) of Ca to the sum total of Ba and Ca is less than 0.2. M<sup>2</sup>  
 Si and germanium -- the sum total -- more than 90mol% -- expressing the included tetravalent element group, Z is an element of -1 value, an element of -2 value, and at least one sort of elements chosen from the group which consists of

H and N.  $0 < b < 0.075$ , c, and d are numbers with which a is satisfied with of  $0.0003 \leq a \leq 0.01$ , and  $1.8 \leq (a+b+c+d) \leq 2.2$ , e, and f are  $[b / 0 < c / (c+d) \leq 0.8, a, b, c, \text{ and } d]$  satisfied of  $0 \leq f / (e+f) \leq 0.035$  and  $3.6 \leq (e+f) \leq 4.4$ .

[Claim 2]

It is \*\* about a rate that the sum total of Ba, Ca, and Sr occupies in  $M^1$  being more than 80mol%.

The fluorescent substance according to claim 1 considered as a mark.

[Claim 3]

Claim 1 or 2, wherein a rate that Si occupies in  $M^2$  is more than 80mol%

It is alike and is a fluorescent substance of a statement.

[Claim 4]

The 1st photogen that generates light of 350 to 430 nm.

The 2nd photogen that generates visible light by the exposure of light from the 1st photogen concerned.

It is the luminescent device provided with the above, and the 2nd photogen contains a fluorescent substance of a statement in any 1 paragraph of claims 1-3.

[Claim 5]

The luminescent device according to claim 4, wherein the 1st photogen is a laser diode or a light emitting diode.

[Claim 6]

A lighting system which has the luminescent device according to claim 4 or 5.

[Claim 7]

An image display device which has the luminescent device according to claim 4 or 5.

[The amendment 2]

[Document to be Amended]Specification

[Item(s) to be Amended]0009

[Method of Amendment]Change

[The contents of amendment]

[0009]

(However, the divalent element excluding  $[M^1]$  a univalent element, Eu, Mn, and Mg, a trivalent element, the average)

The rate that expresses at least one sort of elements chosen as \*\* from the group of a pentavalent element, and a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the rate (mole ratio) of Ca to the sum total of Ba and Ca is less than 0.2.  $M^2$

Si and germanium -- the sum total -- more than 90mol% -- expressing the included tetravalent element group, Z is an element of -1 value, an element of -2 value, and at least one sort of elements chosen from the group which consists of H and N.  $0 < b < 0.075$ , c, and d are numbers with which a is satisfied with of  $0.0003 \leq a \leq 0.01$ , and  $1.8 \leq (a+b+c+d) \leq 2.2$ , e, and f are  $[b / 0 < c / (c+d) \leq 0.8, a, b, c, \text{ and } d]$  satisfied of  $0 \leq f / (e+f) \leq 0.035$  and  $3.6 \leq (e+f) \leq 4.4$ .

[Amendment 3]

[Document to be Amended]Specification

[Item(s) to be Amended]0013

[Method of Amendment]Change

[The contents of amendment]

[0013]

The divalent element excluding  $[M^1]$  in a formula [1] a univalent element, Eu, Mn, and Mg, trivalent origin

Base and at least one sort of elements chosen from the group of a pentavalent element are expressed, The rate that a divalent element occupies is more than 80mol%, Ba, Ca, and the rate that the sum total of Sr occupies are more than 40mol%, and the conditions comparatively (mole ratio) of less than 0.2 of Ca to the sum total of Ba and Ca are fulfilled. When elements other than Ba, Ca, and Sr are described concretely, as a univalent element, They are mentioned by Li, Na, K, Rb, Cs, etc. and as a divalent element, V, Cr, Fe, Co, nickel, Cu, Zn, Mo, Ru, Pd, Ag, Cd, Sn, Sm, Tm, Yb, W, Re, Os, Ir, Pt, Hg, Pb, etc. are mentioned, Although rare earth elements, such as B, aluminum, Ga, In, etc. Y, Sc, are mentioned and P, Sb, Bi, etc. are mentioned as a pentavalent element as a trivalent element, it is not limited to these. In a divalent element, V, Zn, Mo, Sn, Sm, Tm, Yb, W, and Pb are mentioned especially.

[Amendment 4]

[Document to be Amended]Specification

[Item(s) to be Amended]0015

[Method of Amendment]Change

[The contents of amendment]

[0015]

It is preferred that the rate that the sum total of Ba, Ca, and Sr occupies from fields, such as red or white luminescence intensity, is more than 80mol%. It is more preferred that the rate that the sum total of Ba and Ca occupies is more than 80mol%, and it is still more preferred that Ba, Ca, and the percentage that the sum total of Sr occupies are 100-mol%.

$M^2$  in a formula [1] -- Si and germanium -- the sum total -- more than 90mol% -- although the included tetravalent element group is expressed -- fields, such as red or white luminescence intensity, to  $M^2$  -- Si -- more than 80mol% -- containing is preferred and it is more preferred that  $M^2$  consists of Si. As tetravalent elements other than Si and germanium, Zn, Ti, Hf, etc. are mentioned and these may be included from points, such as red or white luminescence intensity, in the range which does not spoil performance.

[Amendment 5]

[Document to be Amended]Specification

[Item(s) to be Amended]0016

[Method of Amendment]Change

[The contents of amendment]

[0016]

Z in a formula [1] is an element of -1 value, an element of -2 value, and at least one sort of elements chosen from the group which consists of H and N. For example, in addition to S, Se, and Te which are the elements of the same -2 value as oxygen, it may be F, Cl, Br, I, etc. which are -1 value, the OH radical may contain, and some oxygen groups

may change to ON group or N basis. Z -- the grade 2 [ about ] with little influence for fluorescence performance, i.e., the elemental ratio for all of an impurity level, -- it may be contained at less than mol%. This is equivalent to 0.035 or less as a mole ratio of Z to (Z+ oxygen atom). Therefore, it is  $0 \leq f/(e+f) \leq 0.035$ , from a point of the performance of a fluorescent substance, as for the range of  $f/(e+f)$  which is a mole ratio of Z to (Z+ oxygen atom),  $f/(e+f) \leq 0.01$  is preferred, and  $f/(e+f) = 0$  is preferred [ the range ] in normal use.

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[Translation done.]